

# Chemistry of Epoxy Compounds. XV.<sup>1</sup> Oxidation of Linoleic Acid with Peracetic and Performic Acid<sup>2</sup>

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The oxidation of monounsaturated fatty materials with organic peracids has been studied extensively and is well understood but similar systematic investigation of polyunsaturated analogs has not been carried out. In the few scattered literature reports (for a review of the literature, see references 3 and 4), purity of starting materials is often unknown and open to serious question, yields of products are low and, of major importance, the nature of the main reaction course is not known with certainty. This note describes the oxidation of a linoleic acid concentrate (90–94% *cis,cis*-9,12-octadecadienoic acid) with peracetic and performic acid. The oxidation reactions were followed quantitatively by measuring consumption of peracid with time and reaction products were isolated and identified.

The oxidation of linoleic acid with peracetic and performic acid proceeds normally, contrary to earlier conclusions.<sup>3,4</sup> With peracetic acid, epoxidation is the predominating reaction. When two moles of peracetic acid is used per mole of linoleic acid, 9,10,12,13-diepoxyoctadecanoic acid is the main product. With one mole of peracetic acid, monoepoxyoctadecanoic acid is obtained. With performic acid (prepared in advance or *in situ*) in excess formic acid, the expected hydroxyformoxy compounds, resulting from the opening of the oxirane rings of diepoxyoctadecanoic acid with formic acid, are obtained. Contrary to expectations, however, hydrolysis of the hydroxyformoxy compounds, diepoxyoctadecanoic acid or the hydroxyacetoxo compounds formed on opening the oxirane rings of diepoxyoctadecanoic acid with acetic acid results in poor yields of the expected tetrahydroxystearic acids. The failure to obtain good yields of tetrahydroxystearic acid on hydrolysis of these intermediates has been reported by others,<sup>5,6</sup> and differs from the usual experience with monoepoxy compounds or their corresponding hydroxyacyloxy compounds, in which quantitative yields of dihydroxy compounds ( $\alpha$ -glycols) can be obtained.

## Experimental

**Starting Material.**—Linoleic acid (composition: 90–94% linoleic, 3–6% oleic, 1% linolenic, 1–3% saturated) was prepared from tobacco seed oil<sup>7</sup> (1100 g.) by mild, rapid hydrolysis,<sup>8</sup> followed by fractional crystallization of the resulting mixture of fatty acids (1030 g.) from acetone (6 ml./g.) at  $-20^{\circ}$  to precipitate saturated acids, and then at  $-50^{\circ}$  (after dilution of the first filtrate to 14 ml./g.) to precipitate oleic acid. These precipitates weighed 125 and 225 g., re-

spectively. Recovery of acetone from the filtrate yielded 660 g. of dark-yellow linoleic acid concentrate, which on distillation through a short Vigreux column yielded 610 g. of almost colorless linoleic acid concentrate, b.p.  $145-160^{\circ}$  (0.005–0.1 mm.),  $n_D^{20}$  1.4673, and iodine number, 171–173. Linoleic acid concentrates of comparable linoleic acid content have also been prepared from corn oil or safflower oil fatty acids by the urea complex precipitation technique, thereby eliminating the low-temperature crystallizations.<sup>9</sup>

Peracetic acid in acetic acid solution was prepared as described earlier.<sup>10</sup> Performic acid was usually prepared and utilized *in situ*.<sup>4</sup>

**Epoxidation of Linoleic Acid with Peracetic Acid.** (a) 9,10,12,13-Diepoxyoctadecanoic Acid.—Twenty-eight grams of linoleic acid (iodine number 172; 0.19 mole of double bond) was placed in a 1-l. three-neck flask immersed in an ice-bath. When the contents had cooled to  $10-15^{\circ}$ , approximately 390 g. of 0.6–0.7 *M* peracetic acid in acetic acid solution was added to supply 0.23–0.27 mole of peracid (20–0% excess over that required for both double bonds). The peracid was added within 2–3 minutes, with efficient stirring, while the reaction temperature was maintained at  $20^{\circ}$ . Samples were removed every hour and the consumption of peracetic acid was followed quantitatively.<sup>4</sup> After 5 hours approximately 0.19 mole of peracetic acid had been consumed and its rate of consumption had become negligible. (Within 2 hours after the reactants were mixed, 0.17 mole of peracetic acid had been consumed.) The reaction mixture was then poured into several volumes of an ice-water mixture. The white fine granular solid which precipitated was filtered with suction and washed on the funnel with several liters of cold water. After it was dry, the crude reaction product weighed 28.6 g., m.p.  $59-67^{\circ}$ , oxirane oxygen, 7.1%<sup>11</sup>; neut. equiv. 315; sapon. equiv. 295, iodine number 2–16, ester content about 4%. Its composition was oxiranocompounds 80%; hydroxyacyloxy compounds, 4%; oxidized, 8%; saturated substances originally present in the starting material, 1–3%, unaccounted for, 5–7%.

The crude reaction product was crystallized twice from acetone, the first time at  $-20^{\circ}$  (2 ml./g.) and the second at  $0^{\circ}$  (5 ml./g.), yielding 10 g. of 9,10,12,13-diepoxyoctadecanoic acid, m.p.  $77.8-78.2^{\circ}$  (lit.  $79^{\circ}$ )<sup>12</sup> oxirane oxygen 9.1%, neut. equiv. 315 (calcd.: oxirane oxygen 10.2%, ut. equiv. 312).

(b) Monoepoxyoctadecanoic Acid.—The epoxidation experiment described above was repeated except that 0.1 mole of peracetic acid (5% excess over that required for one double bond) was employed for 28 g. (0.19 mole of double bond) of linoleic acid. After three hours, consumption of peracid became negligible (0.097 mole consumed) and the reaction mixture was poured into a mixture of ice and water. The solid which separated was dissolved in ether and the ether solution was washed acid-free and dried over calcium sulfate. The non-volatile residue obtained after evaporation of the ether was a straw-colored oil and consisted mainly of monoepoxyoctadecanoic acid, 28 g.; iodine number 85, oxirane oxygen 4.38%, neut. equiv. 305, sapon. equiv. 280 (calculated for monoepoxyoctadecanoic acid: iodine number 86, oxirane oxygen 5.41%, neut. and sapon. equiv. 296).

Crystallization of monoepoxyoctadecanoic acid from acetone (2 ml./g.) at  $-50^{\circ}$  yielded about 10 g. of precipitate (liquid at room temperature). This was recrystallized three times at  $-20^{\circ}$  yielding 0.4 g. of 9,10,12,13-diepoxyoctadecanoic acid, m.p.  $74-77^{\circ}$ , and neut. equiv. 317. A mixed melting point with authentic 9,10,12,13-diepoxyoctadecanoic acid showed no depression.

**Hydroxylation of Linoleic Acid with Performic Acid.**—Performic acid was prepared by mixing 30.5 g. of 25.2% hydrogen peroxide (0.23 mole) with 275 g. of 98–100% formic acid in a three-neck flask and allowing the solution to stand for one hour at room temperature ( $26^{\circ}$ ). The flask and contents were immersed in an ice-bath and 28 g. (0.19 mole of double bond) of linoleic acid was added all at once with efficient agitation (in larger scale runs the linoleic acid was added dropwise). After a short induction period,

- (1) For paper XIV, see *THIS JOURNAL*, **74**, 6139 (1952).
- (2) Presented at the Spring Meeting of the American Chemical Society, Kansas City, Missouri, March 24–April 1, 1954.
- (3) D. Swern, *Chem. Rev.*, **45**, 1 (1949).
- (4) D. Swern, "Organic Reactions," Vol. VII, Chapter 7, John Wiley and Sons, Inc., New York, N. Y., 1953.
- (5) A. F. McKay and A. R. Bader, *J. Org. Chem.*, **13**, 75 (1948).
- (6) T. G. Green and T. P. Hilditch, *Biochem. J.*, **29**, 1552 (1935).
- (7) R. W. Riemenschneider, R. M. Speck and E. G. Beinhart, *Oil & Soap*, **22**, 120 (1945).
- (8) D. Swern, H. B. Knight, T. J. Scanlan and W. C. Ault, *ibid.*, **22**, 302 (1945).

- (9) D. Swern and W. E. Parker, *J. Am. Oil Chemists' Soc.*, **30**, 5 (1953).
- (10) T. W. Findley, D. Swern and J. T. Scanlan, *THIS JOURNAL*, **67**, 412 (1945).
- (11) D. Swern, T. W. Findley, G. N. Billen and J. T. Scanlan, *Anal. Chem.*, **19**, 414 (1947).
- (12) W. C. Smit, *Rec. trav. chim.*, **49**, 675 (1930).

the reaction became strongly exothermic and the reaction mixture became homogeneous. The temperature was maintained between 25–30°. After two hours, consumption of peracid became negligible and the reaction mixture was poured into several volumes of a mixture of ice and water in a separatory funnel. The oil which separated was dissolved in ether and the ether solution was washed free of acid and dried. Evaporation of the ether yielded 36 g. of a pale-yellow viscous oil consisting predominantly of dihydroxydiformoxystearic acid; neut. equiv. 389, iodine number 3 (calculated: neut. equiv. 404, iodine number 0).

Substantially identical results were obtained when hydrogen peroxide (2.5–20% excess), formic acid and linoleic acid were mixed, and the performic acid prepared and utilized *in situ* at 40°. With small excesses (2.5–5%) of hydrogen peroxide, reaction times were usually about 6 hours. The iodine numbers of the crude reaction products were 3 or less, indicating stoichiometric utilization of hydrogen peroxide, but some hydrolysis of formate ester occurred because of the longer reaction time.

Hydrolysis of the hydroxyformoxy compounds at room temperature for 24 hours or under reflux for 5 minutes to several hours with 1 to 6 *N* aqueous sodium hydroxide fol-

lowed by acidification at room temperature or 100° with dilute aqueous hydrochloric acid yielded yellow oils with neutralization equivalents in the range of 330–350 (calculated for tetrahydroxystearic acid 348). Attempted solution of these oils in ether yielded a small quantity of insoluble white solid (about 2 g. from 28 g. of oil), identified as 9,10,12,13-tetrahydroxystearic acid, m.p. 145–147° (lit. 148°, 146°) and neut. equiv. 350.

NOTE ADDED IN PROOF.—In the reaction of linolenic (*cis, cis, cis*-9,12,15-octadecatrienoic) acid with excess perbenzoic acid exactly three atoms of active oxygen are consumed per mole of trienoic acid. Ninety per cent. of the consumed oxygen can be shown by analysis to be present in the molecule as oxirane oxygen. Details will be published at some later date.

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